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Enthalpy and heat capacity of $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$ and 0.20)

Tsuyoshi Sato [a], Satoshi Yamazaki [a], Toshiyuki Yamashita [b], Tsuneo Matsui [a,*], Takanori Nagasaki [a]

[a] *Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

[b] *Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-1195, Japan*

Abstract

Enthalpy increment measurements on $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$ and 0.20) were carried out at temperatures between room temperature and 1180 K by the drop method using a high-temperature Calvet micro-calorimeter. The enthalpy increment values were given for $CaTiO_3$ and $(Ca_{0.80}Pu_{0.20})TiO_3$ in polynomial expressions of temperature using Shomate's method. Heat capacity equations obtained in this study were used to derive the thermodynamic functions, namely entropy and free energy function, and to determine the thermodynamic formation values, namely the standard molar enthalpy of formation, the standard molar Gibbs free energy of formation and the standard molar entropy of formation. The Gibbs free energy of formation of $(Ca_{0.80}Pu_{0.20})TiO_3$ was smaller than that of $CaTiO_3$ in the temperature range from room temperature to 1200 K, showing that $(Ca_{0.80}Pu_{0.20})TiO_3$ is thermodynamically more stable than $CaTiO_3$. The thermodynamic stability of $CaTiO_3$ was found to increase by means of Pu substitution for Ca in $CaTiO_3$. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Multi-phase crystalline ceramics that are natural mineral analogues have been developed for use as waste forms for the disposal of high-level nuclear wastes (HLW). In these ceramics, $CaTiO_3$ with perovskite structure is one of the important constituents and can accommodate substitutionally lanthanides (Ln) and actinides (An) from the waste in solid solution. Hence, the thermodynamic properties of the solid solutions of $CaTiO_3$ with Ln and An are of importance to understand the stability of the waste form at high temperatures.

The phase relationship between PuO_{2-x} and $CaTiO_3$ was recently investigated by X-ray diffraction [1]. It was found that Pu was soluble to at least 20 mol% in $CaTiO_3$ prepared in Ar–8% H_2, and that the solubility of Pu in $CaTiO_3$ prepared in air and vacuum was extremely limited (below 5 mol%). The thermal expansion of $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$, 0.05, 0.10, 0.15) was also investigated by high-temperature X-ray diffraction [1]. The structural phase-transition temperature from orthorhombic *Pbnm* to tetragonal $I4/mcm$ (or orthorhombic *Cmcm*) was estimated to be about 1350 K, and was not influenced by Pu doping in $CaTiO_3$.

The high-temperature heat capacities of pure $CaTiO_3$ and $CaTiO_3$ doped with lanthanides (La, Ce and Nd) have been previously measured [2–5]. Two phase transitions were observed in the heat capacity curves. The first transition occurred at about 1380 K and the second one at about 1530 K. Doping of lanthanides in the Ca sites in $CaTiO_3$ appeared to have little influence on the first transition temperature.

In the present study, enthalpy increment measurements on $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$ and 0.20) were carried out at temperatures between room temperature and 1180 K by the drop method, using a high-temperature Calvet micro-calorimeter. Thermodynamic functions, namely heat capacity, entropy and free energy function, and thermodynamic quantities, namely standard molar enthalpy of formation, standard molar Gibbs free

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[*] Corresponding author. Tel.: +81-52 789 4682; fax: +81-52 789 4691.

E-mail address: t-matsui@nucl.nagoya-u.ac.jp (T. Matsui).

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Table 1
Lattice parameters of $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$ and 0.20)

Sample	*a* (nm)	*b* (nm)	*c* (nm)
$CaTiO_3$	0.5442 ± 0.0001	0.7641 ± 0.0001	0.5380 ± 0.0001
$(Ca_{0.80}Pu_{0.20})TiO_3$	0.5645 ± 0.0001	0.7679 ± 0.0001	0.5406 ± 0.0001

energy of formation and standard molar entropy of formation, were derived using these measured enthalpy increment values.

2. Experimental

2.1. Sample preparation

Samples were prepared by high-temperature sintering of pressed pellets of purified $PuO_2, CaCO_3$ and TiO_2 powders, as described in our previous paper [1]. The compositions prepared in this study were $x = 0$ and 0.20 for $(Ca_{1-x}Pu_x)TiO_3$. Sample pellets heated in Ar–8% H_2 were rough-ground and sieved. The grinding and sieving processes were repeated several times until a sufficient amount of granules (125–250 μm diameter) were obtained. $CaTiO_3$ and $(Ca_{0.80}Pu_{0.20})TiO_3$ samples were individually loaded in platinum containers (5.4 mm diameter, 6.0 mm high and 0.1 mm thick). The containers were evacuated, filled with helium gas to about 1.6×10^4 Pa, and sealed. In order to confirm the air-tightness of the containers, they were heated in air, and the weight change was measured. Since no weight increase was observed due to oxidation of the sample, it was confirmed that the containers were completely sealed. A reference sample of α-Al_2O_3 (NBS SRM-720) was also loaded in a platinum container.

2.2. Procedure for enthalpy measurements

The enthalpy increment measurements were carried out by the drop method using a twin-type, high-temperature calorimeter (the Calvet micro-calorimeter model HT-1000 supplied by Setaram). The experimental assembly and procedures were extensively described in earlier studies [6–8]. The differential signal from the thermocouples was amplified and monitored. The acquisition and processing of the signal were carried out using an on-line computer.

The measurement procedure was as follows: a sample was kept at room temperature (298.15 ± 0.05 K) for 30 min in the sample introducer placed above the calorimeter in order to assure thermal equilibrium. The container was then dropped into the calorimeter kept at a given temperature. Three drop-experiments were done for each sample at each temperature. Experiments were carried out in the temperature range 373–1173 K at intervals of 50 K. NBS-alumina (SRM-720) was used as a calibrant.

3. Results and discussion

3.1. Samples

The lattice parameters of the $(Ca_{1-x}Pu_x)TiO_3$ samples prepared in this study are shown in Table 1 and Fig. 1 and are in good agreement with the previous results [1].

3.2. Enthalpy increment

The enthalpy increment, $H_T - H_{298.15}$, of the samples was calculated from the relative values of heat flow measured in the cases of a blank container (with no sample), an Al_2O_3 standard and a sample, and the known enthalpy increment data of the Al_2O_3 standard. Enthalpy increment values are given in Tables 2 and 3, and their graphical representations are shown in Figs. 2(a) and (b). Fig. 2(a) shows that the present results of $CaTiO_3$ are close to the previous result of Guyot et al. [3] (the fitted result, $H_T - H_{273}$, of Guyot et al. [3] was referred to 298.15 K). As shown in Fig. 2(a) for $CaTiO_3$ and Fig. 2(b) for $(Ca_{0.80}Pu_{0.20})TiO_3$, the temperature dependence of the enthalpy increments does not show

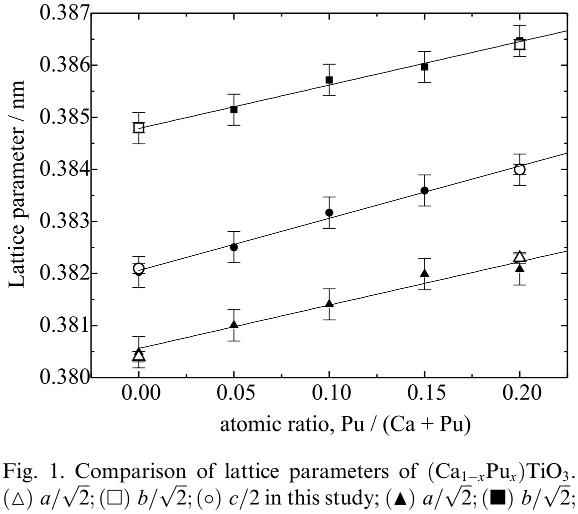

Fig. 1. Comparison of lattice parameters of $(Ca_{1-x}Pu_x)TiO_3$. (△) $a/\sqrt{2}$; (□) $b/\sqrt{2}$; (○) $c/2$ in this study; (▲) $a/\sqrt{2}$; (■) $b/\sqrt{2}$; (●) $c/2$ from the literature [1].

Table 2
Temperature dependence of enthalpy increment of $CaTiO_3$

T (K)	$H_T - H_{298.15,\ \mathrm{exp.}}$ (kJ mol^{-1})	$H_T - H_{298.15,\ \mathrm{cal.}}$ (kJ mol^{-1})	Deviation (%)
376.23	8.119	8.133	−0.17
426.99	13.94	13.79	1.1
477.69	20.09	19.63	2.4
527.93	24.97	25.55	−2.3
578.24	32.02	31.60	1.3
628.48	38.51	37.73	2.1
678.46	45.25	43.90	3.1
728.92	49.91	50.19	−0.56
779.47	55.05	56.55	−2.7
830.50	63.95	63.03	1.5
881.40	67.74	69.53	−2.6
932.09	77.72	76.05	2.2
983.03	81.04	82.64	−1.9
1033.55	94.33	89.21	5.7
1083.84	100.9	95.78	5.3
1133.82	101.9	102.4	−0.4
1133.52	102.6	102.3	0.29
1184.33	111.7	109.0	2.5

Table 3
Temperature dependence of enthalpy increment of $(Ca_{0.80}Pu_{0.20})TiO_3$

T (K)	$H_T - H_{298.15,\ \mathrm{exp.}}$ (kJ mol^{-1})	$H_T - H_{298.15,\ \mathrm{cal.}}$ (kJ mol^{-1})	Deviation (%)
376.23	8.540	8.486	0.63
427.01	14.86	14.46	2.7
477.68	21.03	20.66	1.8
527.93	26.94	26.98	−0.12
578.23	33.27	33.43	−0.46
628.48	40.70	39.97	1.8
678.39	47.53	46.55	2.1
728.93	53.09	53.28	−0.34
779.47	59.62	60.06	−0.73
830.50	66.58	66.97	−0.58
881.40	71.50	73.90	−3.24
932.10	82.06	80.84	1.52
983.03	84.98	87.85	−3.27
1033.56	96.48	94.83	1.74
1083.84	103.1	101.8	1.24
1133.84	107.8	108.8	−0.86
1133.51	108.0	108.7	−0.69
1184.34	115.3	115.8	−0.43

any discontinuity in the temperature range of our measurements. Moreover it has been reported that there is no phase transition of $CaTiO_3$ in the temperature range from room temperature to about 1200 K by calorimetric studies [2–4] and X-ray diffraction measurements [1,9–13]. The $H_T - H_{298.15}$ values at various temperatures were fitted to a polynomial expression in temperature T (K) of the well-known form

$$H_T - H_{298.15} = AT + BT^2 + CT^{-1} + D, \qquad (1)$$

using Shomate's method [14]. The literature value [15] for C_P at 298.15 K of $CaTiO_3$ was used in this regression analysis. The heat capacity at 298.15 K of $(Ca_{0.80}Pu_{0.20})TiO_3$ was calculated using the additivity law from literature values of the heat capacities of $CaTiO_3, PuO_2$ and TiO_2 [15]. The fitted results in the temperature range 373–1173 K are

for $CaTiO_3$:

$$H_T - H_{298.15}\ (\mathrm{J\ mol^{-1}}) = 123.6T + 4.450 \times 10^{-3}T^2 + 2.540 \times 10^{6}T^{-1} - 4.575 \times 10^{4}, \qquad (2)$$

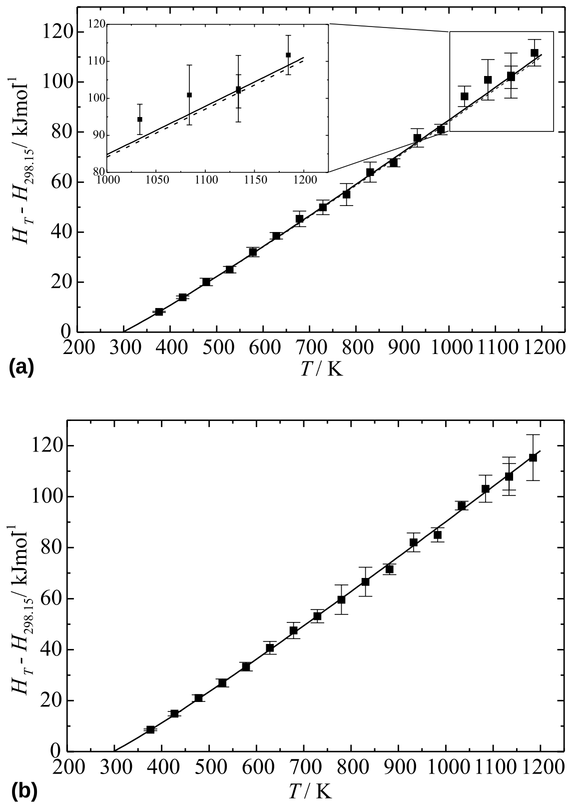

Fig. 2. (a) Temperature dependence of enthalpy increment of $CaTiO_3$ (■ this study; —— regression result; - - - - the fitted value, $H_T - H_{273}$, of Guyot et al. [3] referred to 298.15 K). (b) Temperature dependence of enthalpy increment of $(Ca_{0.80}Pu_{0.20})TiO_3$(■ this study; —— regression result).

for $(Ca_{0.80}Pu_{0.20})TiO_3$:

$$H_T - H_{298.15}\ (\mathrm{J\ mol^{-1}}) = 135.8T + 2.810 \times 10^{-3}T^2 + 3.268 \times 10^6 T^{-1} - 5.169 \times 10^4. \quad (3)$$

These enthalpy increment values are given in Tables 2 and 3. The deviation of the experimental values from the calculated ones is about 3% except for 5% about 1033 and 1083 K.

3.3. Heat capacity

The heat capacity was obtained from the first derivative of Eqs. (2) and (3) with respect to temperature and is given by

for $CaTiO_3$:

$$C_P\ (\mathrm{J\ mol^{-1}\ K^{-1}}) = 123.6 + 8.900 \times 10^{-3}T - 2.540 \times 10^6 T^{-2}, \quad (4)$$

Table 4
Thermodynamic function and quantities of $CaTiO_3$

T (K)	Thermodynamic function of $CaTiO_3$				Thermodynamic quantities of $CaTiO_3$		
	$H_T - H_{298.15}$ (kJ mol^{-1})	C_P (J mol^{-1} K^{-1})	S_T (J mol^{-1} K^{-1})	$-(fef)$ (J mol^{-1} K^{-1})	$\Delta H°_{f,T}$ (kJ mol^{-1})	$\Delta S°_{f,T}$ (J mol^{-1} K^{-1})	$\Delta G°_{f,T}$ (kJ mol^{-1} K^{-1})
298.15	0.00	97.64	93.64	93.64	−1674.05	−0.286	−1588.70
300	0.18	98.01	94.24	93.64	−1674.04	−0.286	−1588.16
400	10.73	111.24	124.51	97.68	−1673.11	−0.286	−1558.72
500	22.22	117.85	150.11	105.67	−1671.60	−0.285	−1529.22
600	34.22	121.84	171.97	114.95	−1669.99	−0.284	−1499.53
700	46.55	124.61	190.98	124.48	−1668.48	−0.283	−1470.41
800	59.12	126.71	207.76	133.86	−1667.93	−0.282	−1442.36
900	71.88	128.43	222.78	142.92	−1667.10	−0.281	−1414.16
1000	84.79	129.92	236.39	151.60	−1666.18	−0.280	−1385.98
1100	97.85	131.25	248.84	159.88	−1665.99	−0.279	−1358.58
1200	111.04	132.48	260.31	167.78	−1652.80	−0.272	−1326.92

for $(Ca_{0.80}Pu_{0.20})TiO_3$:

$$C_P\ (\mathrm{J\ mol^{-1}\ K^{-1}}) = 135.8 + 5.620 \times 10^{-3}T - 3.268 \times 10^{6}T^{-2}. \qquad (5)$$

The smoothed heat capacity values at selected temperatures calculated by Eqs. (4) and (5) are listed in the third column of Tables 4 and 5 and shown in Figs. 3(a) and (b). In Fig. 3(a), the heat capacities calculated using Eq. (4) are compared with the literature values [2,3]. The present result of heat capacity for $CaTiO_3$ falls between the results of Naylor and Cook [2] and Guyot et al. [3]. The maximum difference was about 1% at 600 K. For the heat capacity of $(Ca_{0.80}Pu_{0.20})TiO_3$, there are no published data for comparison. Therefore, the heat capacity was estimated from the additivity law using the present data of $CaTiO_3$ and the literature values of PuO_2 and TiO_2 [15], which are also shown in Fig. 3(b). The present result of $(Ca\ _{0.80}Pu_{0.20})TiO_3$ is about 10% larger than the calculated value in the range 300–1150 K. The

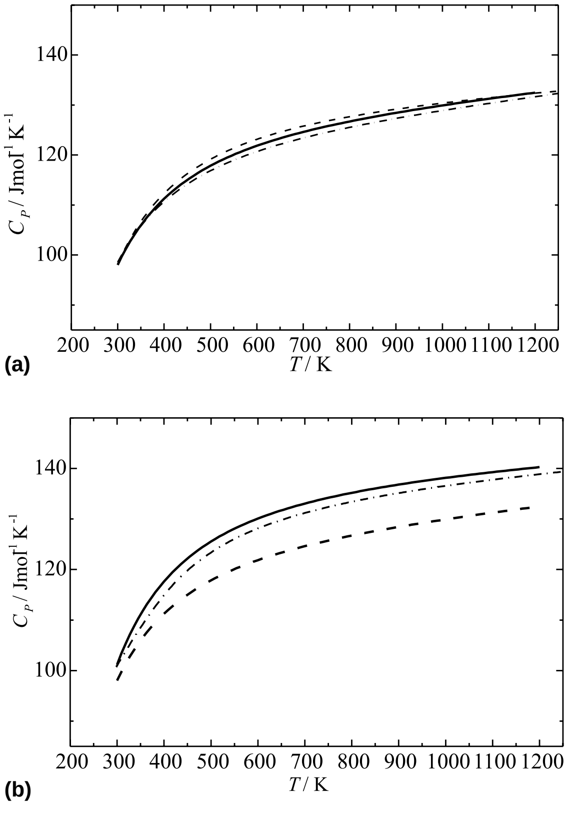

Fig. 3. (a) Temperature dependence of heat capacity of $CaTiO_3$(—— this study; - - - -Naylor and Cook [2]; – · – Guyot et al. [3]). (b) Temperature dependence of heat capacity of $(Ca_{0.80}Pu_{0.20})TiO_3$. —— this study (doped with Pu); - - - - this study (undoped); – · – estimated value from the additivity law (doped with Pu).

Table 5
Thermodynamic function and quantities of $(Ca_{0.80}Pu_{0.20})TiO_3$

Thermodynamic function of $(Ca_{0.80}Pu_{0.20})TiO_3$					Thermodynamic quantities of $(Ca_{0.80}Pu_{0.20})TiO_3$		
T (K)	$H_T - H_{298.15}$ (kJ mol^{-1})	C_P (J mol^{-1} K^{-1})	S_T (J mol^{-1} K^{-1})	$-(fef)$ (J mol^{-1} K^{-1})	$\Delta H^{\circ}_{f,T}$ (kJ mol^{-1})	$\Delta S^{\circ}_{f,T}$ (J mol^{-1} K^{-1})	$\Delta G^{\circ}_{f,T}$ (kJ mol^{-1} K^{-1})
298.15	0.00	100.70	102.36	102.36	−1681.56	−0.280	−1598.21
300	0.19	101.17	102.98	102.36	−1681.56	−0.280	−1597.69
400	11.24	117.61	134.66	106.57	−1686.48	−0.279	−1574.82
500	23.44	125.53	161.85	114.98	−1686.07	−0.278	−1547.07
600	36.24	130.08	185.17	124.78	−1685.67	−0.277	−1519.35
700	49.40	133.05	205.46	134.89	−1684.24	−0.276	−1491.15
800	62.82	135.18	223.37	144.85	−1686.50	−0.275	−1466.85
900	76.42	136.81	239.39	154.48	−1684.73	−0.273	−1438.75
1000	90.17	138.14	253.88	163.71	−1689.08	−0.272	−1416.90
1100	104.04	139.27	267.10	172.51	−1689.06	−0.271	−1390.81
1200	118.02	140.26	279.26	180.91	−1675.09	−0.263	−1359.79

temperature dependence of both samples, however, is seen to be similar. The heat capacity of $(Ca_{0.80}Pu_{0.20})TiO_3$ was larger than that of $CaTiO_3$ in the range 300–1150 K.

3.4. Thermodynamic functions and quantities

The values for the thermodynamic functions for $CaTiO_3$ and $(Ca_{0.80}Pu_{0.20})TiO_3$, calculated from the heat capacity values expressed by Eqs. (4) and (5), are given in Tables 4 and 5, respectively. The entropy value at 298.15 K used for $CaTiO_3$ is the literature value of $CaTiO_3$ [15], and that used for $(Ca_{0.80}Pu_{0.20})TiO_3$ is calculated using the additivity law from the literature values for the entropy of $CaTiO_3, PuO_2$ and TiO_2 [15].

The standard molar enthalpies of formation of these oxides were calculated on the basis of Aronson's semi-empirical equation [16]:

$$\Delta H = -96.5 \sum (X'_A - X'_B)^2, \qquad (6)$$

where X'_A and X'_B are pseudoelectronegativities of metal A and non-metal B, respectively, and the factor 96.5 converts eV/bond to kJ/mol. Using the free energy functions of $CaTiO_3$ obtained from the present study and those of Ca, CaO, Ti, O_2 and TiO_2 from the literature [15] and the standard molar enthalpy of formation, the Gibbs free energy of formation and the standard molar entropy of formation were calculated, and are summarized in Tables 4 and 5.

As seen in Tables 4 and 5, the Gibbs free energy of formation of $(Ca_{0.80}Pu_{0.20})TiO_3$ is smaller than that of $CaTiO_3$ from 298 to 1200 K, indicating that $(Ca_{0.80}Pu_{0.20})TiO_3$ is thermodynamically more stable than $CaTiO_3$. The thermal expansion of $(Ca_{1-x}Pu_x)TiO_3$ was recently investigated by the present authors by high-temperature X-ray diffraction [1]. The thermal expansion coefficients, which can be regarded as important measures of binding energy (and, hence, thermodynamic stability) were found to decrease with increasing Pu content, suggesting that the thermodynamic stability of $CaTiO_3$ is increased by Pu substitution for Ca in $CaTiO_3$. The present results from the enthalpy increment measurements are, therefore, consistent with those from the thermal expansion measurements.

4. Summary

Enthalpy increment measurements on $(Ca_{1-x}Pu_x)TiO_3$ ($x = 0$ and 0.20) were carried out at temperatures between room temperature and 1180 K by the drop method using a high-temperature Calvet micro-calorimeter. Enthalpy increment values were first measured on $(Ca_{0.80}Pu_{0.20})TiO_3$ in this study. The present result for $CaTiO_3$ is close to the previous result of Guyot et al. [3]. Using these measured enthalpy increment values, thermodynamic functions, namely heat capacity, entropy and free energy function, and thermodynamic quantities, namely standard molar enthalpy, entropy and Gibbs free energy of formation, were calculated. The heat capacity data for $CaTiO_3$ fell between the results of Naylor and Cook [2] and of Guyot et al. [3]. The heat capacity of $(Ca_{0.80}Pu_{0.20})TiO_3$ was about 10% larger than that of undoped $CaTiO_3$. The Gibbs free energy of formation of $(Ca_{0.80}Pu_{0.20})TiO_3$ was smaller than that of $CaTiO_3$, showing that $(Ca_{0.80}Pu_{0.20})TiO_3$ was thermodynamically more stable than $CaTiO_3$.

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References

[1] T. Sato, Y. Hanajiri, T. Yamashita, T. Matsui, T. Nagasaki, these Proceedings, p. 130.
[2] B.F. Naylor, O.A. Cook, J. Am. Chem. Soc. 68 (1946) 1003.
[3] F. Guyot, P. Richet, Ph. Coutial, Ph. Gillet, Phys. Chem. Miner. 20 (1993) 141.
[4] K. Nagarajan, Y. Arita, N. Nakamitsu, Y. Hanajiri, T. Matsui, J. Nucl. Mater. 230 (1996) 124.
[5] Y. Arita, K. Nagarajan, T. Ohashi, T. Matsui, J. Nucl. Mater. 247 (1997) 94.
[6] R. Agarwal, K.N. Roy, V. Venugopal, R. Prasad, D.D. Sood, M.L. Jayantkumar, M.R. Ponkshe, BARC/I-875, 1987.
[7] R. Prasad, R. Agarwal, K.N. Roy, V.S. Iyer, V. Venugopal, D.D. Sood, J. Nucl. Mater. 167 (1989) 261.
[8] V.S. Iyer, R. Agarwal, K.N. Roy, S. Venkiteswaran, V. Venugopal, D.D. Sood, J. Chem. Thermodyn. 22 (1990) 439.
[9] C.J. Ball, G.J. Thorogood, E.R. Vance, J. Nucl. Mater. 190 (1992) 298.
[10] X. Liu, R.C. Liebermann, Phys. Chem. Miner. 20 (1993) 171.
[11] S.A.T. Redfern, J. Phys.: Condens. Matter 8 (1996) 8267.
[12] T. Matsui, H. Shigematsu, Y. Arita, Y. Hanajiri, N. Nakamitsu, T. Nagasaki, J. Nucl. Mater. 247 (1997) 72.
[13] B.J. Kennedy, C.J. Howard, B.C. Chakoumakos, J. Phys. Condens. Matt. 11 (1999) 1479.
[14] C.H. Shomate, J. Phys. Chem. 58 (1954) 368.
[15] I. Barin, Thermochemical Data for Pure Substance, VCH, Weinheim, 1989.
[16] S. Aronson, J. Nucl. Mater. 107 (1982) 343.